Carbon Inclusion Compounds

Onion-Type Complexation Based on Carbon Nanorings and a Buckminsterfullerene**

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The construction of onion-type structures, reminiscent of Russian Matrioshka dolls, is a fascinating subject in supramolecular chemistry.[1,2] Although several double-inclusion complexes composed of two host molecules and a metal ion have been described,[3] no examples of double-inclusion complexes composed of three synthetic molecules have been realized to date. Electron microscopy images have proved the existence of various layered carbon networks with curled and closed structures, such as carbon nanotubes[4] and Bucky onions.[5] The spontaneous formation of such new carbon materials with onion-type structures suggests that host molecules with curved conjugated systems would be promising components for the formation of the novel supramolecular structures.[6] Here we report onion-type supramolecular structures based on carbon nanorings and a C_{60} core in nonpolar organic solvents.

Recently we reported the synthesis of cyclic [6]- to [9]paraphenyleneacetylenes ([6]- to [9]CPPA) **1**–**4**. These compounds have smooth belt-shaped structures similar to a cut piece of carbon nanotube, and thus may be termed "carbon nanorings".[7] Moreover, we have found that [6]CPPA (**1**) with a 1.32-nm diameter forms unusually stable inclusion complexes with fullerenes (Figure 1).[8,9] A theoretical calculation predicts that [9]CPPA (**4**) composed of nine *para*-phenyleneacetylene units has a 0.67-nm larger diameter (1.98 nm) than that of **1**. When the van der Waals distance between sp^2 hybridized carbon atoms are taken into account (0.34 nm), **4** is almost perfect complementarity to **1**.

The carbon nanoring **4**[7] and its tribenzo derivative **6**[10] were prepared as mixtures with **1** and **5**, respectively, by the reported procedure.[7,11] These carbon nanorings can be separated by gel permeation chromatography. We found during the purification that the complexes $\mathbf{4}\supset\mathbf{1}$ and $\mathbf{6}\supset\mathbf{5}$ precipitated as yellow solids from a hexane-dichloromethane or benzene solution of the compounds. Both solids are reasonably soluble in chloroform ($CHCl_3$) and dichloromethane (CH_2Cl_2), but poorly soluble in benzene and other solvents. The stoichiometry of these complexes was proved to be 1:1 based on the integration of ^1H NMR spectra recorded in $CDCl_3$. Moreover, the chemical shifts of the protons of each compound in the mixtures resonated at higher magnetic fields than those of the pure forms, and varied according to the concentration and ratio of the compounds (Figure 2). The signals of **5** became broadened below 0 °C, while those of **6** broadened at −60°. The complex $\mathbf{6}\supset\mathbf{5}$ exists as an equilibrium mixture of stereoisomers, and the interconversion, probably by rotation of the aromatic rings, occurs slower than the NMR time scale below these temperatures. These results clearly indicate that inclusion complexes are formed in chloroform solutions. On the other hand, the NMR spectrum of a mixture of [6]-, [7]-, and [8]CPPAs (**1**–**3**) exhibits little spectral changes from their original ones, thus indicating the importance of complementarity in the complexation.

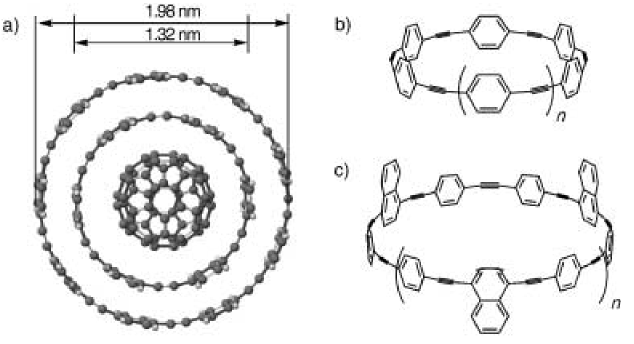

Figure 1. Molecular structures: a) $\mathbf{4}\supset\mathbf{1}\supset C_{60}$, b) CPPAs: **1**: $n=1$, **2**: $n=2$, **3**: $n=3$, **4**: $n=4$, c) **5**: $n=0$, **6**: $n=1$.

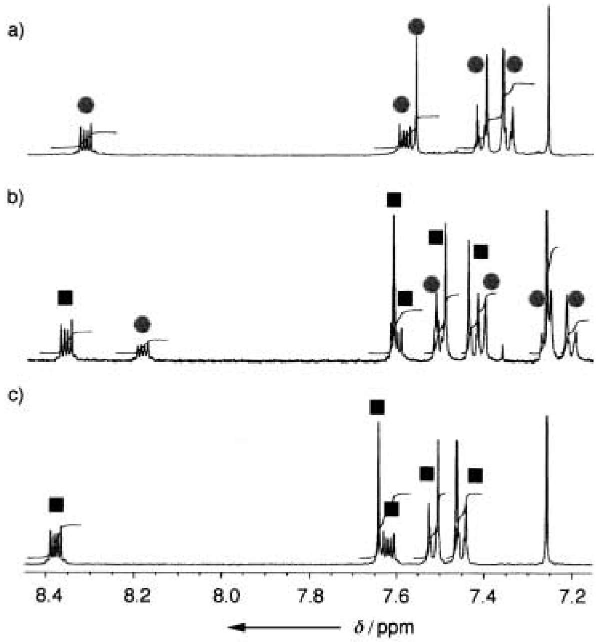

Figure 2. ^1H NMR spectra of a) **5**, c) **6**, and b) their 1:1 complex in $CDCl_3$ at 30 °C. ● represents the signals of **5** and ■ represents the signals of **6**.

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It was regrettable that the precise K_a values of the complex **4**$\supset$**1** were undeterminable except at −60 °C (340 ± 45 L mol^{-1}) because of the relatively low solubility and low K_a values.[12] However, titration experiments with **6**$\supset$**5** in which the variation of the chemical shifts of **6** was monitored enabled the K_a values to be determined at various temperatures (Table 1). The larger K_a values of **6**$\supset$**5** compared to those of **4**$\supset$**1** result from the increase in the contact area. The thermodynamic parameters are calculated from the K_a values. The negative enthalpy and entropy values ($\Delta H = -4.5$ kcal mol^{-1}, $\Delta S = -2.4$ cal mol^{-1} K^{-1}) indicate that substantial attractive forces would drive the host–guest complexation.

Table 1: Association constants (K_a)[a] of **6**$\supset$**5** at various temperatures.[b]

T [°C]	K_a
30	470 ± 80
0	1180 ± 140
−30	3100 ± 200
−60	11000 ± 1400

[a] L mol^{-1}. [b] In CDCl$_3$.

No phenylacetylene macrocycles without electron-withdrawing substituents on their aromatic rings have so far shown such aggregation in nonpolar solvents.[13] The reason for this is that π-π stacking interactions between planar aromatic hydrocarbons causes an electrostatically repulsive force.[14,15] The present results thus show there are substantial differences in the electronic properties between planar and curved conjugated systems. Recent theoretical studies have predicted that the anisotropic distribution of π electrons causes a substantial segregation of electrostatic charge between concave and convex π surfaces.[16–21] The electrostatically attractive forces as well as dispersion forces would be operative between curved conjugated systems. The drastic decrease in the association constants from the fullerene complexes to the nanoring complexes can be attributed to the decrease in the curvature of the corresponding π systems.

The exceptionally high stability of the complexes formed between the carbon nanorings and C$_{60}$ suggests that there is a high probability that double-inclusion complexes (onion-type supramolecular structures) would form. The ^{1}H NMR spectra of **6**$\supset$**5** in the presence of excess C$_{60}$ showed that the signals of **5** and **6** broadened at higher temperatures (**5** at about 30 °C and **6** at 0 °C) than those in the absence of C$_{60}$ (Figure 3 a), which clearly indicates the formation of the onion-type complex **6**$\supset$**5**$\supset$C$_{60}$. The presence of a C$_{60}$ molecule in the cavity of **5** would restrict the interconversion between the stereoisomers (Figure 3 b). Regrettably, the determination of the K_a values by titration experiments of **6** with **5**$\supset$C$_{60}$ by NMR spectroscopy failed because of the extensive broadening of all the signals as the amount of the complex increased. Similar titration experiments of **4** with **1**$\supset$C$_{60}$ at −60 °C enabled the K_a value of **4**$\supset$(**1**$\supset$C$_{60}$) to be successfully determined as 410 ± 80 L mol^{-1}, if it is assumed that **1** complexes nearly perfectly with C$_{60}$ under the reaction conditions.[9] Thus, the K_a value of **4**$\supset$(**1**$\supset$C$_{60}$) is almost identical to that of **4**$\supset$**1** and suggests that the complexation of a fullerene has little effect on the electronic and structual properties of the host **1**.

The attractive interactions would also play an important role in the spontaneous formation of fullerene peapods[22] and other new materials based on carbon nanotubes.[23] Further experimental and theoretical studies on these complexes and related substances will deepen the understanding on the novel nature of fullerenes and other curved π-electron systems.

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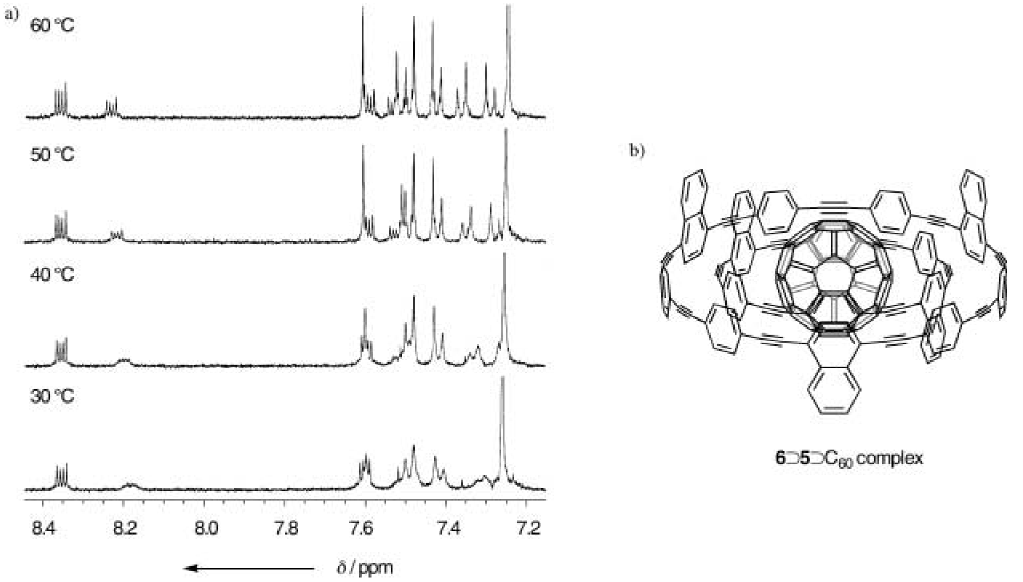

Figure 3. a) Temperature-dependent ^{1}H NMR spectra of **5** and **6** (1:1) in the presence of excess C$_{60}$ in CDCl$_3$. b) A molecular structure of the **6**$\supset$**5**$\supset$C$_{60}$ complex. The complex should exist as an equilibrium mixture of stereoisomers.

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[10] **6**: Yellow fine crystals, m.p. $>210\,^{\circ}$C (decomp under a nitrogen atmosphere); MS (FAB): $m/z = 1050$ [M^+]; IR (KBr): $\tilde{\nu} = 2185$ (C≡C, w), 1512 cm^{-1} (C=C,s); ^{1}H NMR (270 MHz, $CDCl_3$): $\delta =$ 7.45 (AA′BB′, $J_{AB} = 8.4$ Hz, 12H), 7.52 (AA′BB′, $J_{AB} = 8.4$ Hz, 12H), 7.62 (m, naphthyl, 6H), 7.64 (s, 6H), 8.38 ppm (m, naphthyl, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 93.11$, 94.28, 98.08, 122.02, 123.59, 123.72, 126.55, 127.34, 129.83, 131.39 (overlap), 132.99 ppm: UV (cyclohexane): λ_{max} [nm] ($\log \varepsilon$) = 246 (5.05), 385(5.31), 419(4.94); fluorescence (cyclohexane): λ_{max} [nm] = 446, 475.

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